

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/033596 A2

(51) International Patent Classification⁷: C10G 65/04

(21) International Application Number:
PCT/US2003/031740

(22) International Filing Date: 7 October 2003 (07.10.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/416,865 8 October 2002 (08.10.2002) US
60/416,870 8 October 2002 (08.10.2002) US

(71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors: **MURPHY, William, J.**; 16554 Coliseum Avenue, Baton Rouge, LA 70816 (US). **CODY, Ian, A.**; 19516 Cape Hart Court, Baton Rouge, LA 70810 (US).

(74) Agents: **KLIEBERT, Jeremy, J.** et al.; ExxonMobil Research and Engineering Company, 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/033596 A2

(54) Title: A METHOD FOR MAKING LUBE BASESTOCKS

(57) Abstract: A method to produce high quality lube oil products involving hydrotreating a waxy feed to produce a hydrotreated feed and subsequently hydrodewaxing the hydrofinishing the waxy feed.

A METHOD FOR MAKING LUBE BASESTOCKS

FIELD OF THE INVENTION

[0001] This invention relates to a process for preparing lubricating oil basestocks having a high viscosity index (VI) from wax containing feeds. More particularly, a wax containing feedstock is hydrotreated under mild conditions, catalytically hydrodewaxed and hydrofinished.

BACKGROUND OF THE INVENTION

[0002] Historically, lubricating oil products for use in applications such as automotive engine oils have used additives to improve specific properties of the basestocks used to prepare the finished products. With the advent of increased environmental concerns, the performance requirements for the basestocks themselves have increased. American Petroleum Institute (API) requirements for Group II basestocks include a saturates content of at least 90%, a sulfur content of 0.03 wt.% or less and a viscosity index (VI) between 80 and 120. The requirements for Group III basestocks are those of Group II basestocks except that the VI is at least 120.

[0003] Conventional techniques for preparing basestocks such as hydrocracking or solvent extraction require severe operating conditions such as high pressure and temperature or high solvent:oil ratios and high extraction

-2-

temperatures to reach these higher basestock qualities. Either alternative involves expensive operating conditions and low yields.

[0004] Hydrocracking has been combined with hydrotreating as a preliminary step. However, this combination also results in decreased yields of lubricating oils due to the conversion to distillates that typically accompany the hydrocracking process.

[0005] It would be desirable to have a economical process for preparing Group III basestocks in high yields by minimizing conversion to low boiling distillates while at the same time producing a product having excellent low temperature properties, high VI and high stability.

SUMMARY OF THE INVENTION

[0006] The present invention is directed at a process to prepare lubricating oil basestocks having a VI of about 110 to about 130 from a lube oil boiling range feedstock.

[0007] The process comprises:

- a) conducting a lubricating oil feedstock to a solvent extraction zone and underextracting the lubricating oil feedstock under conditions effective at producing at least an aromatics-lean raffinate solution;
- b) removing at least a portion of the extraction solvent from the aromatics-lean raffinate solution to produce a raffinate feedstock having a dewaxed oil viscosity index from about 75 to about 105 and a wax content of greater than 15 wt.%;
- c) contacting the raffinate feedstock with a hydrotreating catalyst in a first reaction stage operated under effective conditions to produce at least a gaseous product and a hydrotreated feedstock
- d) stripping the hydrotreated feedstock to separate at least a portion of the gaseous product from the hydrotreated feedstock to produce a stripped feedstock; and

-4-

- e) contacting the stripped feedstock with at least one dewaxing catalyst in a dewaxing zone operated under effective hydrodewaxing conditions, wherein said dewaxing catalyst contains at least one Group VIII noble metal and is selected from ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, Beta, SSZ-31, SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, fluorided alumina, silica-alumina, fluorided silica alumina, synthetic Ferrierites, Mordenite, Offretite, erionite, chabazite, and mixtures thereof thereby producing a lubricating oil basestock.

[0008] In one embodiment of the present invention, a hydrofinished lubricating oil basestock is produced by contacting the lubricating oil basestock with a hydrofinishing catalyst in a hydrofinishing zone operated under effective hydrofinishing conditions.

DETAILED DESCRIPTION OF THE INVENTION

[0009] It should be noted that the terms "feedstock" and "feedstream" as used herein are synonymous.

Lubricating Oil Feedstocks

[0010] The feedstock used in the process of the invention are wax-containing feeds that boil in the lubricating oil range, typically having a 10% distillation point greater than 650°F (343°C), measured by ASTM D 86 or ASTM 2887, and are derived from mineral sources, synthetic sources, or a mixture of the two. Non-limiting examples of suitable lubricating oil feedstocks include those derived from sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, and Fischer-Tropsch waxes.

[0011] These feedstocks may also have high contents of nitrogen- and sulfur-contaminants. Feeds containing up to 0.2 wt.% of nitrogen, based on feed and up to 3.0 wt.% of sulfur can be processed in the present process. Feeds having a high wax content typically have high viscosity indexes of up to 200 or more. Sulfur and nitrogen contents may be measured by standard ASTM methods D5453 and D4629, respectively.

Raffinate Feedstocks

[0012] The raffinate feedstocks used herein are derived from a solvent extraction process. In a solvent extraction process as contemplated herein, the lube oil feedstocks defined above are solvent extracted. The solvent extraction process selectively dissolves the aromatic components in an aromatics-rich extract solution while leaving the more paraffinic components in the "aromatics-lean raffinate solution". Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrrolidone. By controlling the solvent to oil ratio, extraction temperature and method of contacting distillate to be extracted with solvent, one can control the degree of separation between the extract and raffinate phases.

[0013] In the solvent extraction process, the lube oil feedstocks are subjected to solvent extraction in a solvent extraction zone. In the solvent extraction zone, a lube oil boiling range feedstock as defined above, is contacted with an extraction solvent. The extraction solvent used herein is not critical and can be any solvent known that has an affinity for aromatic hydrocarbons in preference to non-aromatic hydrocarbons. Non-limiting

-7-

examples of such solvents include sulfolane, furfural, phenol, and N-methyl pyrrolidone ("NMP"). Furfural, phenol, and NMP are preferred.

[0014] The contacting of the lube oil boiling range feedstream with the extraction solvent can be accomplished by any suitable solvent extraction method. Non-limiting examples of such include batch, semi-batch, or continuous. It is preferred that the extraction process be a continuous process, and it is more preferred that the continuous process be operated in a counter-current fashion. In a counter-current configuration, it is preferred that the lube oil boiling range feedstream be introduced into the bottom of an elongated contacting zone or tower and caused to flow in an upward direction while the extraction solvent is introduced at the top of the tower and allowed to flow in a downward direction, counter-current to the upflowing lube oil boiling range feedstream. In this configuration, the lube oil boiling range feedstream is forced to pass counter-currently to the extraction solvent resulting in the intimate contact between the extraction solvent and the lube oil boiling range feedstock. The extraction solvent and the lube oil boiling range feedstream thus migrate to opposite ends of the contacting zone.

-8-

[0015] The contacting of the lube oil boiling range feedstream with the extraction solvent produces at least an aromatics-lean raffinate solution. The aromatics-lean raffinate solution is then treated to remove at least a portion of the extraction solvent contained therein, thus producing the raffinate used as a feedstock herein. The removal of at least a portion of the extraction solvent can be done by any means known in the art effective at separating at least a portion of an extraction solvent from an aromatics lean raffinate solution. Preferably the raffinate is produced by separating at least a portion of the first extraction solvent from the aromatics-lean raffinate solution in a stripping or distillation tower. By at least a portion, it is meant that at least about 80 vol%, preferably about 90 vol%, more preferably 95 vol%, based on the aromatics-lean raffinate solution, of the extraction solvent is removed from the aromatics-lean raffinate solution. Most preferably substantially all of the extraction solvent is removed.

[0016] It should be noted that the phrase "aromatics-lean raffinate solution" is not synonymous with the "raffinate". The phrase "aromatics-lean raffinate solution" is meant to refer to the products of solvent extraction before the solvent has been removed, i.e. distilled or stripped, from the respective phases. Thus, "raffinate", as used herein, refers to the raffinate product after at least a

-9-

portion of the solvent contained in the "aromatics-lean raffinate solution has been removed.

[0017] It is preferred that the raffinates used herein be under extracted, i.e., the extraction is carried out under conditions such that the raffinate yield is maximized while still removing most of the lowest quality molecules from the feed. Raffinate yield may be maximized by controlling extraction conditions, for example, by lowering the solvent to oil treat ratio and/or decreasing the extraction temperature. The raffinate from the solvent extraction unit is stripped of solvent and then sent to a hydrotreating unit (zone) containing a hydrotreating catalyst.

[0018] The raffinate feedstock to the hydrotreating zone is extracted to a dewaxed oil viscosity index of from about 75 to about 105, preferably 80 to 95, more preferably about 80 to about 85. The raffinate feedstock will also have a wax content greater than about 15 wt.% wax, preferably greater than about 40 wt.% wax. The wax content of a feed may be determined by nuclear magnetic resonance spectroscopy (ASTM D5292), by correlative ndM methods (ASTM D3238) or by solvent means (ASTM D3235).

-10-

Hydrotreating

[0019] For hydrotreating, the catalysts are those effective for hydrotreating such as catalysts containing at least one metal selected from Group VI metals, Group VIII metals, and mixtures thereof. Preferred metals include nickel, tungsten, molybdenum, cobalt and mixtures thereof. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. The amount of metals, either individually or in mixtures, for supported catalysts ranges from about 0.5 to 35 wt.%, based on the catalyst, while if a bulk or unsupported catalyst is used, the metals content can range as high as 98 wt.%, based on the catalyst. In the case of preferred mixtures of Group VIII metals with Group VI metals, the Group VIII metals are present in amounts ranging from about 0.5 to 5 wt.%, based on catalyst and the Group VI metals are present in amounts ranging from about 5 to 30 wt.%. The amounts of metals may be measured by atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectrometry or other methods specified by ASTM for individual metals.

[0020] The hydrotreating catalysts used herein can be either supported, or bulk or unsupported. However, if the hydrotreating catalyst is supported, it is important that the metal oxide support used for the hydrotreating catalysts

-11-

herein be non-acidic so as to control cracking. A useful scale of acidity for catalysts is based on the isomerization of 2-methyl-2-pentene as described by Kramer and McVicker, J. Catalysis, 92, 355 (1985). In this scale of acidity, 2-methyl-2-pentene is subjected to the catalyst to be evaluated at a fixed temperature, typically 200°C. In the presence of catalyst sites, 2-methyl-2-pentene forms a carbenium ion. The isomerization pathway of the carbenium ion is indicative of the acidity of active sites in the catalyst. Thus weakly acidic sites form 4-methyl-2-pentene whereas strongly acidic sites result in a skeletal rearrangement to 3-methyl-2-pentene with very strongly acid sites forming 2,3-dimethyl-2-butene. The mole ratio of 2-methyl-2-pentene to 4-methyl-2-pentene can be correlated to a scale of acidity, which ranges from 0.0 to 4.0. Very weakly acidic sites will have values near 0.0 whereas very strongly acidic sites will have values approaching 4.0. The catalysts useful in the present process have acidity values of less than about 0.5, preferably less than about 0.3. The acidity of metal oxide supports can be controlled by adding promoters and/or dopants, or by controlling the nature of the metal oxide support, e.g., by controlling the amount of silica incorporated into a silica-alumina support. Examples of promoters and/or dopants include halogen, especially fluorine, phosphorus, boron, yttria, rare-earth oxides and magnesia. Promoters such as halogens generally increase the acidity of metal

-12-

oxide supports while mildly basic dopants such as yttria or magnesia tend to decrease the acidity of such supports.

[0021] Suitable metal oxide supports include low acidic oxides such as silica, alumina or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or beta having average pore sizes from 50 to 200Å, preferably 75 to 150Å, a surface area from 100 to 300 m²/g, preferably 150 to 250 m²/g and a pore volume of from 0.25 to 1.0 cm³/g, preferably 0.35 to 0.8 cm³/g. The supports are preferably not promoted with a halogen such as fluorine as this generally increases the acidity of the support above 0.5.

[0022] Preferred metal catalysts include cobalt/molybdenum (1-5% Co as oxide, 10-25% Mo as oxide) nickel/molybdenum (1-5% Ni as oxide, 10-25% Co as oxide) or nickel/tungsten (1-5% Ni as oxide, 10-30% W as oxide) on alumina. Especially preferred are nickel/molybdenum catalysts such as KF-840.

[0023] Effective hydrotreating conditions as used herein typically include temperatures of from 150 to 400°C, preferably 200 to 350°C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), preferably 2859 to

-13-

13891 kPa (400 to 2000 psig), a space velocity of from 0.1 to 10 liquid hourly space velocity (LHSV), preferably 0.1 to 5 LHSV, and a hydrogen to feed ratio of from 89 to 1780 m³/m³ (500 to 10000 scf/B), preferably 178 to 890 m³/m³.

[0024] Hydrotreating reduces the amount of nitrogen- and sulfur-containing contaminants to levels that will not unacceptably affect the dewaxing catalyst in the subsequent dewaxing step. Also, there may be certain polynuclear aromatic species that will pass through the present mild hydrotreating step. These contaminants, if present, will be removed in a subsequent hydrofinishing step.

[0025] Effective hydrotreating conditions are considered those conditions which when selected, result in less than 5 wt.% of the feedstock, preferably less than 3 wt.%, more preferably less than 2 wt.%, being converted to 650°F (343°C) minus products. Effective hydrotreating conditions are also those that when selected produce a hydrotreated feedstock whose VI increase is less than 4, preferably less than 3, more preferably less than 2 greater than the VI of the feedstock. The high wax contents of the present feeds results in minimal VI increase during the hydrotreating step.

-14-

[0026] The hydrotreated feedstock may be passed directly to the dewaxing step or preferably, stripped to remove gaseous contaminants such as hydrogen sulfide and ammonia prior to dewaxing. Stripping can be by conventional means such as flash drums or fractionators.

Dewaxing Catalyst

[0027] The dewaxing catalyst may be either crystalline or amorphous. Crystalline materials are molecular sieves that contain at least one 10 or 12 ring channel and may be based on aluminosilicates (zeolites) or on aluminophosphates such as silicoaluminophosphates (SAPO's) and MAPO's. Zeolites used for oxygenate treatment may contain at least one 10 or 12 channel. Examples of such zeolites include ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, ferrierite, ITQ-13, MCM-68 and MCM-71. Examples of aluminophosphates containing at least one 10 ring channel include ECR-42. Examples of molecular sieves containing 12 ring channels include zeolite beta, and MCM-68. The molecular sieves are described in US Patent Numbers 5,246,566, 5,282,958, 4,975,177, 4,397,827, 4,585,747, 5,075,269 and 4,440,871. MCM-68 is described in US Patent No. 6,310,265. MCM-71 and ITQ-13 are described in PCT published applications WO 0242207 and WO 0078677. ECR-42 is disclosed in US 6,303,534. Suitable SAPO's for use

-15-

herein include SAPO-11, SAPO-31, SAPO-41, and suitable MAPO's include MAPO-11. SSZ-31 is also a catalyst that can be effectively used herein.

Preferred catalysts include ZSM-48, ZSM-22 and ZSM-23. Especially preferred is ZSM-48. The molecular sieves are preferably in the hydrogen form. Reduction can occur in situ during the dewaxing step itself or can occur ex situ in another vessel.

[0028] Amorphous dewaxing catalysts include alumina, fluorided alumina, silica-alumina, fluorided silica-alumina and silica-alumina doped with Group IIIB metals. Such catalysts are described for example in US Patent Nos. 4,900,707 and 6,383,366. The dewaxing catalysts used herein are bifunctional, i.e., they are loaded with at least one metal hydrogenation component, which is selected from Group VI metals, Group VIII metals, or mixtures thereof. Preferred metals are selected from Group VIII metals. Especially preferred are Group VIII noble metals such as Pt, Pd or mixtures thereof. These metals are loaded at the rate of 0.1 to 30 wt.%, based on catalyst. Catalyst preparation and metal loading methods are described for example in US Patent No. 6,294,077, and include for example ion exchange and impregnation using decomposable metal salts. Metal dispersion techniques and catalyst particle size control

-16-

techniques are described in US Patent No. 5,282,958. Catalysts with small particle size and well-dispersed metal are preferred.

[0029] The molecular sieves are typically composited with binder materials which are resistant to high temperatures which may be employed under dewaxing conditions to form a finished dewaxing catalyst or may be binderless (self bound). The binder materials are usually inorganic oxides such as silica, alumina, silica-aluminas, binary combinations of silicas with other metal oxides such as titania, magnesia, thoria, zirconia and the like and tertiary combinations of these oxides such as silica-alumina -thoria and silica-alumina magnesia. The amount of molecular sieve in the finished dewaxing catalyst is from 10 to 100, preferably 35 to 100 wt.%, based on catalyst. Such catalysts are formed by methods such spray drying, extrusion and the like. The dewaxing catalyst may be used in the sulfided or unsulfided form, and is preferably in the sulfided form.

[0030] Effective dewaxing conditions as used herein includes temperatures of from 250 - 400°C, preferably 275 to 350°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), preferably 1480 to 17339 kPa (200 to 2500 psig), liquid hourly space velocities of from 0.1 to 10 hr⁻¹, preferably 0.1 to 5 hr⁻¹ and

-17-

hydrogen treat gas rates from 45 to 1780 m³/m³ (250 to 10000 scf/B), preferably 89 to 890 m³/m³ (500 to 5000 scf/B).

Hydrofinishing

[0031] In a preferred embodiment, at least a portion of the product from dewaxing is passed directly to a hydrofinishing step without disengagement. It is preferred to hydrofinish the product resulting from dewaxing in order to adjust product qualities to desired specifications. Hydrofinishing is a form of mild hydrotreating directed to saturating any lube range olefins and residual aromatics as well as to removing any remaining heteroatoms and color bodies. The post dewaxing hydrofinishing is usually carried out in cascade with the dewaxing step. Generally the hydrofinishing will be carried out at temperatures from about 150°C to 350°C, preferably 180°C to 250°C. Total pressures are typically from 2859 to 20786 kPa (about 400 to 3000 psig). Liquid hourly space velocity is typically from 0. 1 to 5 LHSV (hr⁻¹), preferably 0. 5 to 3 hr⁻¹ and hydrogen treat gas rates of from 44.5 to 1780 m³/m³ (250 to 10,000 scf/B).

[0032] Hydrofinishing catalysts are those containing at least one metal selected from Group VI metals, Group VIII metals, and mixtures thereof. Preferred metals include at least one noble metal having a strong hydrogenation

-18-

function, especially platinum, palladium and mixtures thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt.% or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts for aromatics saturation will comprise at least one metal having relatively strong hydrogenation function on a porous support. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. Noble metals are usually present in amounts no greater than about 1 wt.%.

[0033] The hydrofinishing catalyst is preferably a mesoporous material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica contents whose preparation is further described in J. Amer. Chem. Soc., 1992, 114, 10834. Examples included MCM-41, MCM-48 and MCM-50. Mesoporous refers to catalysts having pore sizes from 15 to 100 Å. A preferred member of this class is MCM-41 whose preparation is described in US Patent No. 5,098,684. MCM-41 is an inorganic, porous, non-layered phase having a hexagonal arrangement of uniformly-sized pores. The physical structure of MCM-41 is

-19-

like a bundle of straws wherein the opening of the straws (the cell diameter of the pores) ranges from 15 to 100 Angstroms. MCM-48 has a cubic symmetry and is described for example in US Patent No. 5,198,203 whereas MCM-50 has a lamellar structure. MCM-41 can be made with different size pore openings in the mesoporous range. The mesoporous materials may bear a metal hydrogenation component which is at least one Group VIII metal. Preferred are Group VIII noble metals, most preferably Pt, Pd or mixtures thereof.

[0034] As stated above, typical hydrofinishing conditions include temperatures from about 150°C to 350°C, preferably 180°C to 250°C. Total pressures are typically from 2859 to 20786 kPa (about 400 to 3000 psig). Liquid hourly space velocity is typically from 0.1 to 5 LHSV (hr^{-1}), preferably 0.5 to 3 hr^{-1} and hydrogen treat gas rates of from 44.5 to 1780 m^3/m^3 (250 to 10,000 scf/B). Effective hydrofinishing conditions, as used herein, are conditions within the above-defined ranges that when used in conjunction with the selected hydrofinishing catalyst results in a lubricating oil product meeting the desired specifications, i.e. color, etc.

[0035] The lubricating oil basestocks resulting from the presently disclosed process will have viscosity indexes ("VI") of about 110 to about 130,

-20-

preferably about 115 to about 125. These basestocks will also have excellent volatility and low temperature properties.

[0036] The above description is directed to preferred embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0037] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

EXAMPLES

EXAMPLE 1

[0038] A raffinate having a Viscosity Index ("VI") of 90, (following solvent dewaxing) and having a wax content of 15wt.% was used to produce a basestock having a dewaxed oil VI of 115. The raffinate was hydrotreated at 370°C, hydrogen pressure of 1800 psi, and liquid hourly space velocities ("LHSV") of 0.35 hr⁻¹. The raffinate was hydrotreated with a commercial catalyst obtained from Akzo Nobel and marketed under the name KF-840. The results of this Example are contained in Table 1 below.

EXAMPLES 2 AND 3

[0039] It should be noted that the Examples that follow, namely Examples 2 and 3, are based on information derived from models and estimates from related experiments. These examples illustrate approaches to upgrading a raffinate to 115 VI but instead using a combination of hydrotreating and hydrodewaxing. (A hydrofinishing step would normally be used in a commercial process but was not considered germane to demonstrating the invention) The catalyst used for hydrodewaxing comprises a noble metal on a bound zeolite (ZSM-48).

[0040] The key properties of the solvent dewaxed basestock are the relationship between the kinematic viscosity and volatility and formulated oil low temperature properties. A volatility of less than 15% Noack is excellent for a viscosity of 4.5 cSt @ 100C. The Mini-Rotary Viscosity (MRV) in a 5W30 formulation was measured at 35,000 cP.

EXAMPLE 2

[0041] The raffinate used in this Example was the same as described in Example 1 above. The hydrotreating conditions included temperatures of 360-380°C, pressures up to 2500 psig and liquid hourly space velocities ("LHSV") of 0.2 to 2 hr⁻¹, along with utilizing the same KF-840 catalyst of Example 1. The hydrodewaxing conditions needed to achieve the target pour point of -18°C are in the range 330 to 340°C for a process operating at 1800 psi H₂ and at a LHSV of 1.0 v/v/hr.

[0042] Thus, in this Example, the raffinate was hydrotreated to produce a hydrotreated raffinate having a VI of 108. The hydrotreated raffinate was then dewaxed under the conditions described above to produce a basestock having a VI of 115. The results of this Example are contained in Table 1, below.

EXAMPLE 3

[0043] As mentioned above, Example 3 also used a two step process involving hydrotreating under conditions similar to those outlined in Example 1 above followed by hydrodewaxing. However, the raffinate used in this Example was an underextracted raffinate having a wax content of 15wt.% and

-23-

a VI of 83 (dewaxed oil basis). The hydrodewaxing conditions were similar to those described above in Example 2.

[0044] In this Example, the underextracted raffinate was hydrotreated to produce a hydrotreated underextracted raffinate having a VI of 108. The hydrotreated underextracted raffinate was then hydrodewaxed to produce a basestock having a VI of 115. The results of this Example are contained in Table 1; below.

TABLE 1

	Example 1 Hydrotreating only	Example 2 Hydrotreating + Hydrodewaxing	Example 3 Hydrotreating + Hydrodewaxing
Raffinate, Feed VI	90	90	83
Hydrotreating (DWO VI Target)	115	108	108
Basestock Properties			
VI (Viscosity Index)	115	115	115
Viscosity, 100°C cSt	4.5	4.7	4.5
Noack Volatility, %	14.5	16	14.5
Formulated Oil			
MRV, cP	35,000	20,000	20,000
Yield	Base	+	++

-24-

[0045] The yield of Example 1 was used as a standard yield for comparison of the yields of Examples 2 and 3.

[0046] The data contained in Table 1 also illustrates that the process of Example 2 using a raffinate that is not underextracted produces a basestock having excellent Noack volatility at the given viscosity and excellent low temperature properties as defined by Formulated Oil Mini Rotary Viscosity (MRV) of 20,000cP. Table 1 also illustrates that the low temperature properties of the formulated oil of Example 2 are substantially improved versus Example 1, however the viscosity/ volatility relationship is poorer. Example 2 also demonstrated an increased yield over that obtained by hydrotreating only (Example 1).

[0047] The data contained in Table 1 also illustrates that the process of Example 3 using an under-extracted raffinate produces a basestock having excellent Noack volatility at viscosity and excellent low temperature properties as defined by Formulated Oil Mini Rotary Viscosity (MRV) of 20,000cP. Thus, Table 1 shows that the product of Example 3 has both excellent low temperature properties and an excellent viscosity/volatility relationship. This also results in an increased yield over that obtained by hydrotreating and

-25-

hydrodewaxing the standard raffinate illustrated in Example 2. Example 3 shows the benefit of utilizing an under-extracted raffinate in a combined hydrotreating-hydrodewaxing process.

[0048] Thus, these Examples demonstrate that by using an underextracted raffinate, a refiner can produce superior yields of basestocks having excellent Noack volatility and low temperature properties than by using a raffinate that is not underextracted.

-26-

CLAIMS:

1. A process to prepare lubricating oil basestocks having a VI of at least about 110 to about 130 from a lube oil boiling range feedstock comprising:
 - a) conducting a lubricating oil feedstock to a solvent extraction zone and underextracting the lubricating oil feedstock under conditions effective at producing at least an aromatics-lean raffinate solution;
 - b) removing at least a portion of the extraction solvent from the aromatics-lean raffinate solution to produce a raffinate feedstock having a dewaxed oil viscosity index from about 75 to about 105 and a wax content of greater than 15 wt.%;;
 - c) contacting the raffinate feedstock with a hydrotreating catalyst in a first reaction stage operated under effective conditions to produce at least a gaseous product and a hydrotreated feedstock;
 - d) stripping the hydrotreated feedstock to separate at least a portion of the gaseous product from the hydrotreated feedstock to produce a stripped feedstock; and
 - e) contacting the stripped feedstock with at least one dewaxing catalyst in a dewaxing zone operated under effective hydrodewaxing conditions, wherein said dewaxing catalyst

-27-

contains at least one Group VIII noble metal and is selected from ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, Beta, SSZ-31, SAPO-11, SAPO-31, SAPO-41, MAPO-11, ECR-42, fluorided alumina, silica-alumina, fluorided silica alumina, synthetic Ferrierites, Mordenite, Offretite, erionite, chabazite, and mixtures thereof thereby producing a lubricating oil basestock.

2. The process of claim 1 wherein the hydrotreating catalyst contains at least one metal selected from Group VI metals, Group VIII metals, and mixtures thereof.
3. The process of claim 1 wherein the dewaxing catalyst is at least one catalyst selected from ZSM-22, ZSM-23, ZSM-48, and ZSM-57.
4. The process of claim 1 wherein the dewaxing catalyst is ZSM-48.
5. The process of claim 1 wherein the dewaxing catalyst is sulfided, reduced, or sulfided and reduced.

-28-

6. The process of claim 1 wherein the lubricating oil basestock is contacted with a hydrofinishing catalyst in a hydrofinishing zone operated under effective hydrofinishing conditions to produce a hydrofinished lubricating oil basestock.

7. The process of claim 6 wherein the hydrofinishing catalyst contains at least one metal selected from Group VI metals, Group VIII metals, and mixtures thereof.

8. The process of claim 6 wherein the hydrofinishing is selected from mesoporous catalysts from the M41S family.

9. The process according to claim 1 wherein said effective dewaxing conditions include temperatures of from 250 - 400°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), liquid hourly space velocities of from 0.1 to 10 hr⁻¹, and hydrogen treat gas rates from 45 to 1780 m³/m³ (250 to 10000 scf/B).

10. The process according to claim 9 wherein said effective hydrotreating conditions include temperatures of from 150 to 400°C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), a space velocity of

-29-

from 0.1 to 10 liquid hourly space velocity (LHSV), and a hydrogen to feed ratio of from 89 to 1780 m³/m³ (500 to 10000 scf/B).

11. The process according to claim 1 wherein the dewaxing catalyst contains at least one metal selected from Pt, Pd, and mixtures thereof.
12. The process according to claim 8 wherein the hydrofinishing catalyst further comprises at least one noble metal.
13. The process according to claim 1 wherein said hydrotreating catalyst is a hydrotreating catalyst selected from bulk and supported hydrotreating catalysts.
14. The process according to claim 13 wherein said hydrotreating catalyst is a supported hydrotreating catalysts having a support selected from low acidic metal oxide supports.
15. The process according to claim 14 wherein said low acidic metal oxide supports are selected from silica, alumina and titania.

-30-

16. The process according to claim 13 wherein said hydrotreating catalyst has an acidity value of less than about 0.5, as determined by the scale of acidity for catalysts described by Kramer and McVicker, J. Catalysis, 92, 355 (1985).

17. The process according to claim 10 wherein said effective hydrotreating conditions are selected such that less than 5 wt.% of the feedstock is converted to 650°F (343°C) minus products and wherein the VI increase of said hydrotreated feedstock is less than 4 greater than the VI of the lube oil boiling range feedstock.

18. The process according to claim 1 wherein said lubricating oil feedstock has a 10% distillation point greater than 650°F (343°C), as measured by ASTM D 86 or ASTM 2887, and is derived from mineral sources, synthetic sources, and mixtures of the two.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/033596 A3

- (51) International Patent Classification⁷: **C10G 65/04**
- (21) International Application Number:
PCT/US2003/031740
- (22) International Filing Date: 7 October 2003 (07.10.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/416,865 8 October 2002 (08.10.2002) US
60/416,870 8 October 2002 (08.10.2002) US
- (71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).
- (72) Inventors: **MURPHY, William, J.**; 16554 Coliseum Avenue, Baton Rouge, LA 70816 (US). **CODY, Ian, A.**; 19516 Cape Hart Court, Baton Rouge, LA 70810 (US).
- (74) Agents: **KLIEBERT, Jeremy, J.** et al.; ExxonMobil Research and Engineering Company, 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report:
24 June 2004
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 2004/033596 A3

(54) Title: A METHOD FOR MAKING LUBE BASESTOCKS

(57) Abstract: A method to produce high quality lube oil products involving hydrotreating a waxy feed to produce a hydrotreated feed and subsequently hydrodewaxing the hydrofinishing the waxy feed.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/31740

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C10G65/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C10G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 264 826 B1 (XIAO JIRONG ET AL) 24 July 2001 (2001-07-24) column 4, line 64 - column 7, line 61 column 9, line 3 - column 10, line 51 column 11, line 39 - column 12, line 23 claims; examples 1-4	1-18
X	WO 02/48291 A (EXXONMOBIL RES & ENG CO) 20 June 2002 (2002-06-20) page 6, line 21 - page 12, line 15 claims 1,11-14,24	1-18
A	US 4 636 299 A (BERTOLACINI RALPH J ET AL) 13 January 1987 (1987-01-13) the whole document	1-18
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 28 April 2004		Date of mailing of the international search report 06/05/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016		Authorized officer Dötterl, E

5

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.
PCT/US 03/31740

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	<p>WO 02/099014 A (BENARD GERARD ; DUPREY ERIC (FR); SHELL INT RESEARCH (NL); VAN VEEN JO) 12 December 2002 (2002-12-12) the whole document</p>	1-18

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/US 03/31740

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6264826	B1	24-07-2001	US 5993644 A 30-11-1999
		AU 724570 B2 28-09-2000	
		AU 3716597 A 09-02-1998	
		BR 9710321 A 17-08-1999	
		CA 2260104 A1 22-01-1998	
		CN 1225662 A 11-08-1999	
		CZ 9900097 A3 14-04-1999	
		DE 69724790 D1 16-10-2003	
		EA 850 B1 26-06-2000	
		EP 0912659 A1 06-05-1999	
		HU 0003145 A2 28-02-2001	
		ID 17464 A 08-01-1998	
		JP 2001525861 T 11-12-2001	
		KR 2000023804 A 25-04-2000	
		PL 331039 A1 21-06-1999	
		TR 9900098 T2 21-04-1999	
		WO 9802502 A1 22-01-1998	
WO 0248291	A	20-06-2002	US 2002038777 A1 04-04-2002
			AU 1779302 A 24-06-2002
			CA 2429500 A1 20-06-2002
			WO 0248291 A1 20-06-2002
US 4636299	A	13-01-1987	NONE
WO 02099014	A	12-12-2002	CA 2449348 A1 12-12-2002
			WO 02099014 A2 12-12-2002
			EP 1392799 A2 03-03-2004

THIS PAGE BLANK (USPTO)